# Identical Particle Continued

## I. First excited state of Helium $(z=2)$

$$E^0_{n_1,n_2} = -\frac{mc^2(Z\alpha)^2}{2}\left(\frac{1}{n_1^2}+\frac{1}{n_2^2}\right)$$

$$E^0_{11} = -\frac{4mc^2\alpha^2}{2}(2) = -\frac{8mc^2\alpha^2}{2} = -108.8\ eV$$

$$E^0_{12} = -\frac{4mc^2\alpha^2}{2}\left(1+\frac{1}{4}\right) = -\frac{5mc^2\alpha^2}{2} = -68.0\ eV$$

$\hat{H}' = \frac{e^2}{|\vec{r}_1-\vec{r}_2|}$ rotationally invariant
does not depend on spin

total spin $\vec{S} = \vec{S}_1+\vec{S}_2$
$|\vec{S}|^2$ eigenvalue $0 \le S \le 1$ $S = 0, 1$

$[\hat{H}', \hat{S}^2] = 0$ and $[\hat{H}', \hat{L}^2] = 0 = [\hat{H}', \hat{L}_z]$

Without spin-orbit interaction, L and S are separately conserved.

So $\hat{H}'$ is diagonal in basis $l, m_l, s, m_s$
$|l_1-l_2| \le l \le l_1+l_2$ $l = 0, 1$

$\psi = (\text{space}) \times (\text{spin})$

$(\text{spin}) = \chi_{00}$ (antisymmetric) singlet

or $\chi_{1m_s}$ (symmetric) triplet

$(\text{space}) = \psi_{1s} \otimes (\psi_{2s}$ or $\psi_{2p})$

where –
$\psi_{2s} = \psi_{200}$ singlet
$\psi_{2p} = \psi_{21m_l}$ triplet

total of 4 space × 4 spin = 16 states

totally antisymmetric wave function

$$\psi_+(\text{space})\,\chi_{00} \quad ; \quad \psi_-(\text{space})\,\chi_{1 m_s}$$

$$\psi_\pm(1s,2s) = \frac{1}{\sqrt{2}}\left[\psi_{1s}(1)\psi_{2s}(2) \pm \psi_{1s}(2)\psi_{2s}(1)\right]$$

$$\psi_\pm(1s,2p) = \frac{1}{\sqrt{2}}\left[\psi_{1s}(1)\psi_{2p}(2) \pm \psi_{1s}(2)\psi_{2p}(1)\right]$$

Because $\hat{H}'$ is rotationally invariant

$\langle\psi|\hat{H}'|\psi\rangle$ does not depend on $m_\ell, m_s$.
the $s$ quantum number goes with the opposite symmetry of the spatial wave function: $s=0$ is antisymmetric, $s=1$ is symmetric

| correction | $\ell$ | $s$ | mult. | $\psi$ |
|---|---|---|---|---|
| $E_+'(s,s)$ | 0 | 0 | 1 | $\psi_+(1s,1s)\,\chi_{00}$ |
| $E_-'(s,s)$ | 0 | 1 | 3 | $\psi_-(1s,1s)\,\chi_{1m_s}$ |
| $E_+'(s,p)$ | 1 | 0 | 3 | $\psi_+(1s,2p)\,\chi_{00}$ <br> $m_\ell = -1,0,1$ |
| $E_-'(s,p)$ | 1 | 1 | 9 | $\psi_-(1s,2p)\,\chi_{1m_s}$ <br> $m_\ell = -1,0,1$ <br> $m_s = -1,0,1$ |
| | | | 16 | |

Consider $E_\pm(1s, 2p)$ :

$$E^1_\pm(1s,2p) = \int d^3r_1\, d^3r_2\, \psi_\pm^*(\vec{r}_1,\vec{r}_2) \frac{e^2}{|\vec{r}_1-\vec{r}_2|} \psi_\pm(\vec{r}_1,\vec{r}_2)$$

$$= \frac{1}{2}\int d^3r_1 d^3r_2 \Big\{ \left(\psi_{1s}^*(1)\psi_{2p}^*(2) \pm \psi_{1s}^*(2)\psi_{2p}^*(1)\right)$$

$$\frac{e^2}{|\vec{r}_1-\vec{r}_2|} \left( \psi_{1s}(1)\psi_{2p}(2) \pm \psi_{1s}(2)\psi_{2p}(1) \right)\Big\}$$

$$= \frac{1}{2}\int d^3r_1 d^3r_2 \left[ |\psi_{1s}(1)|^2 |\psi_{2p}(2)|^2 + |\psi_{1s}(2)|^2 |\psi_{2p}(1)|^2 \right] \frac{e^2}{|\vec{r}_1-\vec{r}_2|}$$

$$\pm \frac{1}{2}\int d^3r_1\, r_2 \Big[ \psi_{1s}^*(1)\psi_{2p}^*(2)\psi_{1s}(2)\psi_{2p}(1)$$

$$+ \psi_{1s}^*(2)\psi_{2p}^*(1)\psi_{1s}(1)\psi_{2p}(2) \Big] \frac{e^2}{|\vec{r}_1-\vec{r}_2|}$$

then we can exchange dummies $\vec{r}_1, \vec{r}_2$

$$= \int d^3r_1 d^3r_2\, |\psi_{1s}(1)|^2 |\psi_{2p}(2)|^2 \frac{e^2}{|\vec{r}_1-\vec{r}_2|}$$

$$\pm \int d^3r_1 d^3r_2\, \psi_{2p}^*(2)\psi_{1s}(2) \frac{e^2}{|\vec{r}_1-\vec{r}_2|} \psi_{2p}(1)\psi_{1s}^*(1)$$

$\equiv J \pm K$ J, K both manifestly is positive and all $\psi_{21m_\ell}$ will give same number.

$J = 13.2\,eV$ , $K = 0.9\,eV$

$$E_\pm = \underbrace{E^0_{12}}_{=-13.6*2^2(1+1/4)=-68.0} + J \pm K = (-54.8 \pm 0.9)\,eV$$

Similarly $E'_{\pm}(1s,2s) = J' \pm K' = (11.4 \pm 1.2)\,eV$

*where +/- refers to K,K′ is exchange energy*

E(1S,2S) = -56.6+/-1.2
E(1S,2P) = -54.8+/- 0.9 eV

Experiment

1S-2S -58.8+/-0.4 eV
1S-2P -57.9+/-0.25 eV

*K from Commins*

*calculated values, from Townsned/Powell, Crassmann Quantum Mechanics, 1961*

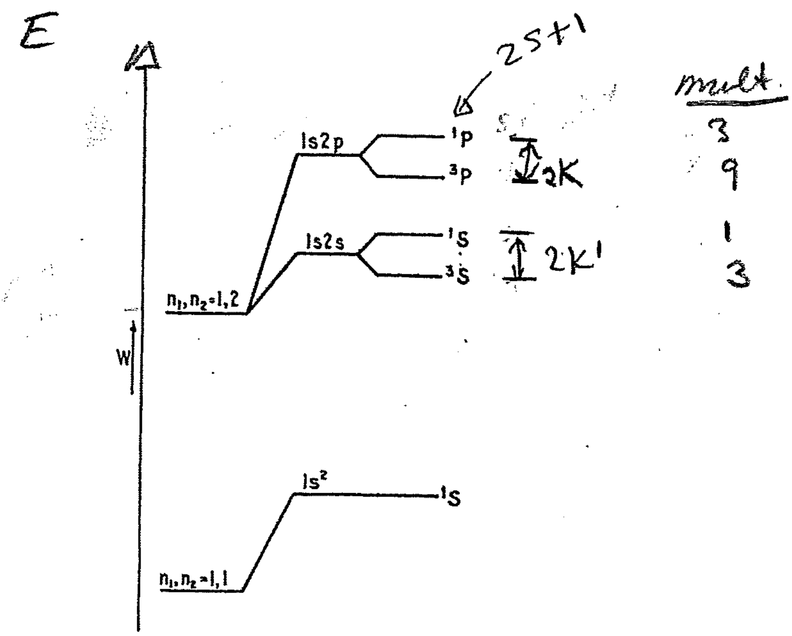



FIG. 29-1.—The splitting of energy levels for the helium atom.

From Pauling & Wilson

example of Hund's rule 1:
1. states with highest S have lower energy

## A bit about multielectron atoms

$$\hat{H} = \sum_{i=1}^{Z} \left( \frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right) + V_c + V_{so} + V_{ss}$$

Coulomb, spin-orbit, spin-spin

$$V_c = \sum_{\text{pairs } i,j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

Anti-symmetrized zeroth order wave function by Slater-Determinant!

$$\Psi^{(0)} = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_a(1) & \psi_a(2) & \cdots & \psi_a(n) \\ \psi_b(1) & \psi_b(2) & \cdots & \psi_b(n) \\ \vdots & & & \\ \psi_n(1) & \psi_n(2) & \cdots & \psi_n(n) \end{vmatrix}$$

state label

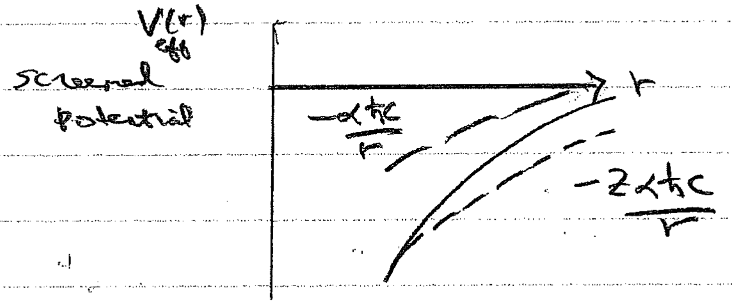
particle label

For example, He ground state

$$\Psi = \frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_{1s}(1)\uparrow_1 & \psi_{1s}(1)\downarrow_1 \\ \psi_{1s}(2)\uparrow_2 & \psi_{1s}(2)\downarrow_2 \end{vmatrix}$$

$$= \psi_{1s}(1)\,\psi_{1s}(2)\,\frac{1}{\sqrt{2}}\left(\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2\right)$$

Independent particle model: each electron moves in effective screened potential




$$V(r) \cong \frac{e^2}{r}\left[Z - \int_0^r d^3r'\,\rho(r')\right]$$

↑ all other electrons

Some computational schemes: statistical model, Hartree's self-consistent field

$$V_i(r_i) = -\frac{Ze^2}{r_i} + \sum_{j\neq i}\int d^3r_j\,\left|\psi_j(\vec{r}_j)\right|^2 \frac{e^2}{r_{ij}}$$

$V_c(r)$ does not go like $1/r$, so states of given $n$ with different $l$ are no longer degenerate.

Closed subshell ($l$) is spherically symmetric

$$\sum_{m=-l}^{+l}\left|Y_{lm}\right|^2 = \frac{2l+1}{4\pi}$$

Electron shells

closed sub-shell= Nobel gases

| n | shell (n) | # states $= 2n^2$ | Configuration |
|---|---|---|---|
| 1 | K | 2 | $1s^2$ |
| 2 | L | 8 | $2s^2 2p^6$ |
| 3 | M | 18 | $3s^2 3p^6 3D^{10}$ |
| 4 | N | 32 | $4s^2 4p^6 4D^{10} 4F^{14}$ |

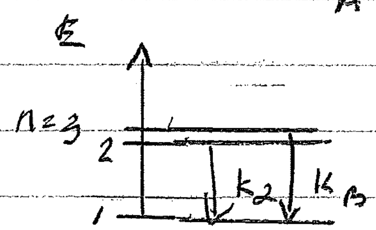
K-shell electron see screened nuclear charge

$$E_{1s} \cong (Z-1)^2(-13.6\,eV)$$

Moseley (1913) determined Z of element Al(13) - Ag(47) by mono-energetic $e^-$ scattering:

$$e^- + A_A^Z = (A_A^Z)^{+*} + 2e^-$$

$$\hookrightarrow (A_A^Z)^+ + \gamma_K$$



observed $\sqrt{f} \sim (Z-1)$

$$\Delta E = h f_N = (-13.6)(Z-1)^2\left(1 - \frac{1}{n^2}\right)$$

order in periodic table by chemical property explained by nuclear charge Z!

Valence ≡ # extra / missing $e^-$ in outer shell

Nobel (inert) gases have filled outer shells

recall $R_{nl} \xrightarrow[r \to 0]{} r^l$

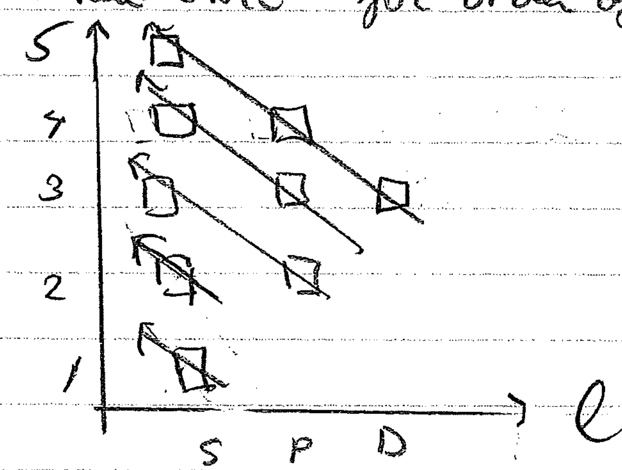
higher l states are pushed out, experience more screening, are less tightly bound.

$$E_{n,s} < E_{n,p} < E_{n,D}$$

$Ar\ (Z=18)$: $1s^2 2s^2 2p^6 3s^2 3p^6$

$1^{st}$ break $K(Z=19) = [Ar]\, 4s$ atomic configuration

Useful mnemonic for order of electron




atomic configuration chart

Nobel gases appear in large peaks in plot of ionization energy vs Z

| | | |
|---|---|---|
| He | $1s^2$ | closed K |
| Li | [He]2s | |
| ⋮ | | |
| Ne | $[He]2s^2 2p^6$ | closed L |
| Na | [Ne] 3s | |
| ⋮ | | closed M |
| Ar | $[Ne]\,3s^2\,3p^6$ | |
| K | [Ar] 4s | |
| ⋮ | filled first | |
| Kr | $[Ar]\,4s^2\,3d^{10}\,4p^6$ | closed N |
| Rb | [Kr] 5s | |

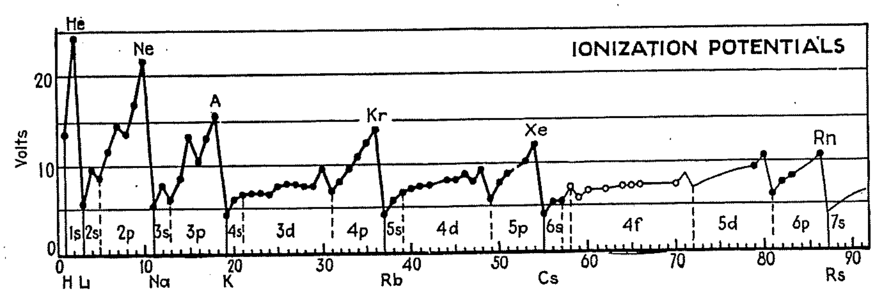



**Figure 8-4** Ionization potential for the outermost electron of each element. (From *Introduction to Atomic Spectra* by Harvey E. White. Copyright 1934 by McGraw-Hill Book Company. Used with permission.)

Ground state wave functions of "optically active" electrons (in outer subshell)
refer to Commins.

Approximation scheme:

① j-j coupling assume spin orbit dominate

$$\vec{J}_i = \vec{L}_i + \vec{S}_i \qquad \vec{J} = \sum \vec{J}_i$$

② L-S coupling (Russell-Saunders)
assume electrostatic interaction dominate spin orbit. works well for all but highest Z atoms.

$$H^0 = \sum_{i=1}^{Z} \left( \frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \sum_{i \neq j} \frac{e^2}{r_{ij}}$$

with $r_{ij} \equiv |\vec{r}_i - \vec{r}_j|$

Both L, S are good quantum numbers.

$$[\vec{S}, H^0] = 0$$

$$[\vec{L}, H^0] = 0$$

proof for 2 electrons, $\vec{L} = \vec{L}_1 + \vec{L}_2$

with $\vec{L} = \vec{L}_1 + \vec{L}_2$

$$[\vec{L}_1, H^0] = e^2\left[\vec{r}_1 \times \vec{p}_1, \frac{1}{r_{12}}\right]$$

$$= e^2 \vec{r}_1 \times \left[\vec{p}_1, \frac{1}{r_{12}}\right]$$

$$\left[p_{x_1}, \frac{1}{r_{12}}\right] = (-i\hbar)\frac{\partial}{\partial x_1}\left[(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2\right]^{-1/2}$$

$$= (-i\hbar)\left(-\tfrac{1}{2}\right)2\,\frac{(x_1-x_2)}{r_{12}^3}$$

so $$\left[\vec{p}_1, \frac{1}{r_{12}}\right] = i\hbar\left(\frac{\vec{r}_1-\vec{r}_2}{r_{12}^3}\right)$$

and $$[L_1, H^0] = e^2\frac{i\hbar}{r_{12}^3}\,\vec{r}_1 \times (\vec{r}_1 - \vec{r}_2)$$

$$= \frac{-i\hbar e^2}{r_{12}^3}\,\vec{r}_1 \times \vec{r}_2$$

also, $$[\vec{L}_2, H^0] = \frac{-i\hbar}{r_{12}^3}\,\vec{r}_2 \times \vec{r}_1$$

so $$[\vec{L}_1 + \vec{L}_2, H^0] = 0$$

degeneracy of outer shell with quantum number $l$, all states filled is

$$d_l = 2(2l+1)$$

example: carbon $Z=6$ $[C] = 1s^2 2s^2 2p^2$

2 of 6 $l=1$ states filled, number of ways of filling 6 states is

$$\frac{6!}{(6-2)!} = 30$$

but identical electrons given 2 equivalent, so

$$d_1(n=2) = \frac{6!}{2!(6-2)!} = 15$$

generalizing,

$$d_l(n) = \frac{(2(2l+1))!}{n!\,(2(2l+1)-n)!} = \binom{2(2l+1)}{n}$$

Binomial coefficient

States with given $l, s, j$ are called **terms**.

for carbon $l = l_1 \oplus l_2 = 2 + 1 + 0$

$s = \frac{1}{2} \oplus \frac{1}{2} = 1 + 0$

total multiplicity $= (3 \times 3) \times (2 \times 2) = 36$

not all allowed by Pauli exclusion.

$j = (3+2+1) + (2+1+0) + 1 + (2+1+0)$

mult. $= (7+5+3) + (5+3+1) + 3 + (5+3+1) = 36$ ✓

States with specific $l, s$ are refered to as multiplets. Making a multiplet table you can determine the term, $^{2S+1}L_j$. "term symbol" Some terms are excluded by the Pauli exclusion principle. Due to spin-orbit, spin-spin interactions they have different energies. The ground-state term is determined by Hund's rules.

example $[O] = 1s^2 2s^2 2p^4$

ground state multiplet $^3P = \underbrace{{}^3P_2 + {}^3P_1 + {}^3P_0}_{\text{terms}}$

ground state term

Here sub-shell $4 > \frac{1}{2}(6)$ greater than ½ full

Hund's rule #3 : $j = l+s = 2$ lowest.

On HW #8, you make a multiplet table for Carbon, finding Pauli allowed terms and use Hund's rules to determine ground state. You will also learn graphical short-cut technique to get ground state term.

## Hund's Rules (Gasiorowicz)

① State with largest $s$ lies lowest

② for given $s$, state with max $\ell$ lowest

③ for given $\ell, s$

subshell $< \frac{1}{2}$ full $\quad j = |\ell - s|$ lowest

subshell $> \frac{1}{2}$ full $\quad j = \ell + s$ lowest

① largest spin state is symmetric
spatial state anti-symmetric reduces overlaps

② higher $\ell$ wave function has more lobes, reducing overlaps

③ reduces spin-orbit coupling

Spin-Orbit for 1 extra electron in $\ell$=1 orbital

$$\hat{H}_{so} = -\vec{\mu} \cdot \vec{B}' = \frac{eg}{2mc} \vec{S} \cdot \vec{B}' \qquad \vec{\mathcal{E}} = -\vec{\nabla}\phi \qquad V = -e\phi$$

$$\vec{\nabla} V = \frac{\hat{r}}{r}\frac{dV}{dr} \qquad \vec{B}' = -\frac{1}{c}\vec{v} \times \vec{\mathcal{E}} = \frac{-1}{ec}\vec{v} \times \vec{\nabla} V$$

Thomas presession

$$\hat{H}_{so} = \frac{1}{2}\frac{e}{mc}\vec{S} \cdot \left[\frac{-1}{ec}\vec{v} \times \left(\frac{\vec{r}}{r}\frac{dV}{dr}\right)\right]$$

$g=2$

$$= -\frac{1}{2}\frac{1}{m^2c^2}\vec{S} \cdot \vec{p} \times \frac{\vec{r}}{r}\frac{dV}{dr} = +\frac{1}{2m^2c^2}\vec{S} \cdot \vec{L}\,\frac{1}{r}\frac{dV}{dr}$$

$$\langle \hat{H}_{so} \rangle = \frac{+1}{2m^2c^2}\langle \vec{L} \cdot \vec{S} \rangle \left\langle \frac{1}{r}\frac{dV}{dr} \right\rangle$$

$$= \frac{+1}{4m^2c^2}\left[j(j+1) - \ell(\ell+1) - s(s+1)\right]\left\langle \frac{1}{r}\frac{dV}{dr} \right\rangle$$

Since $\langle \frac{1}{r}\frac{dV}{dr} \rangle > 0$ lowest $j$ has lowest energy
for shell $> \frac{1}{2}$ filled, absence of electron is
+ charge hole which reverses sign of $\langle \hat{H}_{so} \rangle$.